

Article

## The First Lanthanide Telluride-Bromide: $\text{La}_3\text{Te}_4\text{Br}$ , a Valence Compound

Markus Larres<sup>1</sup>, Anja-Verena Mudring<sup>2</sup> and Gerd Meyer<sup>1,\*</sup>

<sup>1</sup> Department für Chemie, Universität zu Köln, Greinstraße 6, D-50939 Köln, Germany;  
E-Mail: larresm@uni-koeln.de

<sup>2</sup> Fakultät für Chemie, Ruhr-Universität Bochum, D-44780 Bochum, Germany;  
E-Mail: anja.mudring@rub.de

\* Author to whom correspondence should be addressed; E-Mail: gerd.meyer@uni-koeln.de;  
Tel.: +49-221-470-3262; Fax: +49-221-470-5083.

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**Abstract:** The first ternary lanthanide telluride-bromide  $\text{La}_3\text{Te}_4\text{Br}$  was obtained from a mixture of  $\text{LaTe}$  and  $\text{LaBr}_3$  (in the presence of iridium) in a sealed tantalum container at elevated temperatures. The crystal structure (orthorhombic,  $Pnma$ ,  $a = 1634.3(2)$ ,  $b = 435.0(1)$ ,  $c = 1426.6(2)$  pm,  $Z = 4$ ,  $R_1(I_0 > 2\sigma(I_0)) = 0.0349$ ) is built from dicapped trigonal prisms of tellurium and bromine atoms surrounding lanthanum in two different ways. The dicapped trigonal prisms are connected via common edges to a three-dimensional structure, in the same fashion as is known for the binary  $\text{U}_3\text{Te}_5$ .  $\text{La}_3\text{Te}_4\text{Br}$  is a valence compound according to  $(\text{La}^{3+})_3(\text{Te}^{2-})_4(\text{Br}^-)$  and one out of three lanthanide telluride-halides known to date.

**Keywords:** lanthanum; telluride-bromide; synthesis; crystal structure

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### 1. Introduction

There is a remarkable difference in our knowledge of chalcogenide-halides  $\text{RChX}$  of the rare-earth elements (R) when the chalcogen (Ch) part is considered alone; while the oxide-halides  $\text{ROX}$ , the most prolific compound type, are all known and were structurally characterized at least by powder X-ray diffraction, in many cases by single crystal X-ray structure determination, see for example ref. [1],

telluride-halides are almost unknown. It appears that only two compounds in the R/Te/I system have been well characterized, virtually none in the other R/Te/X systems. The two R/Te/I compounds,  $\text{Er}_{17.3}\text{Te}_{24}\text{I}_8$  [2] and  $\text{La}_2\text{TeI}_2$  [3], also mark the two principal alternatives in telluride-halide chemistry. The first, a three-dimensional nonstoichiometric compound, may be derived from the NaCl-type of structure with polytelluride fragments, with tellurium in the oxidation states -2 and -1. The latter,  $\text{La}_2\text{TeI}_2$ , would be counted as a metal-rich layer compound with condensed octahedral clusters; it has the same structure as  $3\text{R-Lu}_2\text{CCl}_2$  [4], better represented as  $\{\text{CLu}_2\}\text{Cl}_2 = \{\text{TeLa}_2\}\text{I}_2$  [5]. Octahedral lanthanum clusters with endohedral tellurium atoms,  $\{\text{TeLa}_{6/3}\}$ , share common edges to double layers which are sheathed by closest packed iodide layers above and below.

Rare-earth element clusters with endohedral atoms of both main-group and transition elements are a steadily growing class of compounds which must be seen in connection with the cluster chemistry of the early transition elements, especially groups 4 through 6 [5-20]. The configuration crossover  $4f^n5d^0 \leftrightarrow 4f^{n-1}5d^1$  of some of the lanthanides allows for bonding interactions between, predominantly, the endohedral atom Z and the cluster atoms R [5,16-19].

There is also a growing number of metal-rich lanthanide tellurides, see especially [18], of which  $\text{Sc}_2\text{Te}$  [20] was one of the first binary examples. The ternary compound  $\text{Sc}_{14}\text{Os}_3\text{Te}_8$  [21] links this chemistry structurally to the reduced rare-earth element chemistry just mentioned.  $\text{Sc}_{14}\text{Os}_3\text{Te}_8$ , or better  $\{\text{Os}_3\text{Sc}_{12}\}\text{Te}_8\text{Sc}_{2-x}$ , has remarkable structural similarities with  $\{\text{Os}_3\text{Sc}_{12}\}\text{Br}_{16}\text{Sc}$  [22]. Both compounds contain the same extended cluster chain of square antiprisms and cubes of scandium atoms (in a 2:1 ratio) with endohedral eight-coordinate osmium atoms! The chains are surrounded by eight telluride (-2) and sixteen bromide (-1) ions, respectively, and additional scandium atoms reside in octahedral interstices between the hexagonally close-packed chains.

One goal of our present research in this area is to combine these two chemistries and create metal-rich condensed-cluster telluride-halides. Consequently, first explorations in the systems Z/R/Te/X were designed for compounds like  $\{\text{Ir}_3\text{R}_{12}\}\text{Br}_8\text{Te}_4$ . Although we have not yet accomplished our goal, we have, in the Ir/La/Te/Br system, obtained the first lanthanide telluride bromide,  $\text{La}_3\text{Te}_4\text{Br}$ .

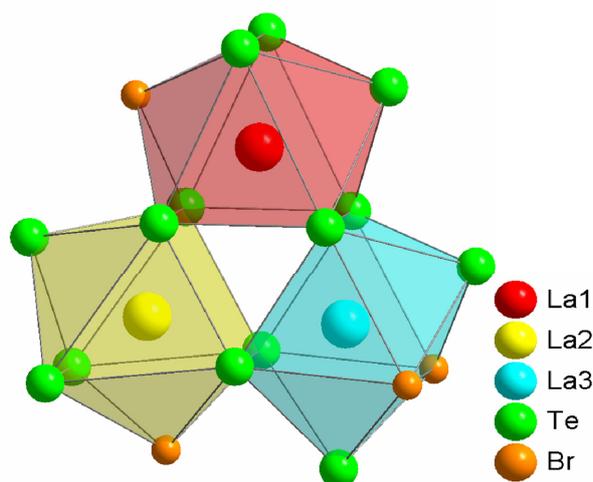
## 2. Results and Discussion

The ternary compound  $\text{La}_3\text{Te}_4\text{Br}$  is obtained from mixtures of  $\text{LaTe}$ ,  $\text{LaBr}_3$  and Ir at elevated temperatures in a sealed tantalum reaction container. The crystal structure of  $\text{La}_3\text{Te}_4\text{Br}$  (orthorhombic, *Pnma*,  $a = 1634.3(2)$ ,  $b = 435.0(1)$ ,  $c = 1426.6(2)$  pm,  $Z = 4$ ) is best regarded as a valence compound, according to  $(\text{La}^{3+})_3(\text{Te}^{2-})_4(\text{Br}^-)$ . All Te—Te distances are at or beyond 377 pm which attests for single non-bonded  $\text{Te}^{2-}$ . For comparison, all bonding distances in  $\text{LaTe}_2$ —which might, roughly, be understood as a metallic ditelluride,  $(\text{La}^{3+})(\text{e}^-)(\text{Te}_2^{2-})$  [23-25]—are between 299 and 341 pm.

As all atoms occupy the Wyckoff site (4c) in the orthorhombic space group *Pnma*, there are as many crystallographically independent atoms in  $\text{La}_3\text{Te}_4\text{Br}$  as the formula claims, with four formula units in the unit cell. All three lanthanum atoms exhibit coordination number eight, with dicapped trigonal prisms as the corresponding polyhedra. La1 and La2 are surrounded by seven tellurium atoms with one tellurium and one bromine atom as the caps of two rectangular faces, and La3 is surrounded by six tellurium and two bromine atoms with the bromine atoms forming one edge of the trigonal prism. The three prisms are connected via two common edges (Te2—Te4 and Te3—Br) to a trimeric

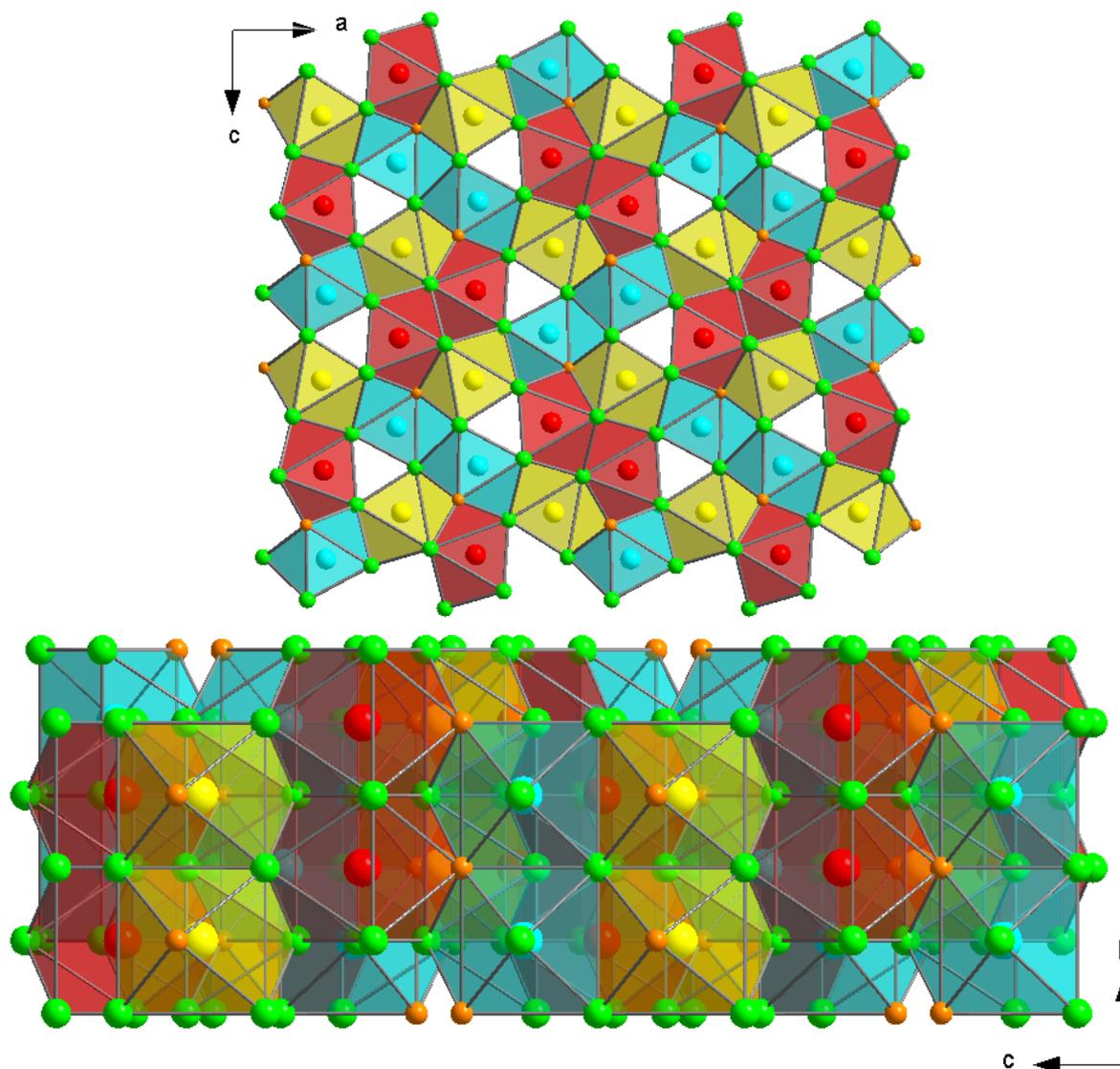
building unit of the composition  $\text{La}_3\text{Te}_{14}\text{Br}_4$ . The  $b$  axis as the short axis, 435.0(1) pm, is identical with the height of the trigonal prisms. Thus, there are Te1—Te1, Te2—Te2, Te3—Te3, Te4—Te4, and Br—Br distances all of this length. Te—Te distances in the triangles and to the caps are usually shorter, starting at 377 pm and going up to 461 pm, see legend to Figure 1. The Te—Te distance in NaCl-type NaTe is 455 pm [23]. There are two bromine functions (terminal and capping) in  $\text{La}_3\text{Te}_4\text{Br}$ , which are reflected in the La—Br distances of 304.60(9) (prism edge) and 310.78(14)/312.74(14) pm (caps). These distances compare quite well with the corresponding distances in  $\text{LaBr}_3$ , 310 (6x) and 316 pm (3x) for the tricapped trigonal prism of its  $\text{UCl}_3$ -type structure [26]. La—La distances within the  $\text{La}_3\text{Te}_{14}\text{Br}_4$  building block are 476.1(1) pm (La1—La2), 456.5(1) pm (La1—La3), and 462.4(1) pm (La2—La3).

**Figure 1.** The building block  $\text{La}_3\text{Te}_{14}\text{Br}_4$  in the crystal structure of  $\text{La}_3\text{Te}_4\text{Br}$ : the three crystallographically independent La atoms (La1: red; La2: yellow; La3: blue) and their surrounding by Te and Br atoms. Interatomic distances in pm and angles in degrees (with estimated standard deviations in parentheses): La1—Br1 = 310.78(14), La1—Te2<sup>(i)</sup> = 329.26(8), La1—Te2 = 329.26(8), La1—Te4<sup>(ii)</sup> = 329.55(8), La1—Te4<sup>(iii)</sup> = 329.55(8), La1—Te4 = 333.37(11), La1—Te3<sup>(iv)</sup> = 337.46(8), La1—Te3 = 337.46(8), La2—Br1<sup>(ii)</sup> = 312.74(14), La2—Te3<sup>(iiii)</sup> = 327.98(8), La2—Te3<sup>(v)</sup> = 327.98(8), La2—Te2 = 329.77(11), La2—Te4 = 330.64(8), La2—Te4<sup>(vi)</sup> = 330.64(8), La2—Te1 = 333.88(8), La2—Te1<sup>(i)</sup> = 333.88(8), La3—Br1<sup>(vi)</sup> = 304.60(9), La3—Br1 = 304.60(9), La3—Te1<sup>(vii)</sup> = 325.38(8), La3—Te1<sup>(viii)</sup> = 325.38(8), La3—Te2<sup>(viii)</sup> = 328.20(8), La3—Te2<sup>(x)</sup> = 328.20(8), La3—Te3 = 332.88(11), La3—Te1<sup>(xi)</sup> = 337.01(11). Operators for generating equivalent atoms: (i)  $x, y+1, z$ ; (ii)  $-x, -y, -z+1$ ; (iii)  $-x, -y+1, -z+1$ ; (iiii)  $-x+1/2, -y, z-1/2$ ; (v)  $-x+1/2, -y-1, z-1/2$ ; (vi)  $x, y-1, z$ ; (vii)  $x, y+1, z+1$ ; (viii)  $x, y, z+1$ ; (viii)  $-x+1/2, -y, z+1/2$ ; (x)  $-x+1/2, -y-1, z+1/2$ ; (xi)  $-x, -y-1, -z+1$ .



The building blocks  $\text{La}_3\text{Te}_{14}\text{Br}_4$  as exhibited in Figure 1 are connected such that each of the tellurium atoms have five lanthanum neighbors and each of the bromine atoms has four direct lanthanum neighbors, such that the connectivities might be written as follows,  $\text{La}_3(\text{Te}_{7/5})_2\text{Te}_{6/5}\text{Br}_{4/4} = \text{La}_3\text{Te}_{20/5}\text{Br}_{4/4} = \text{La}_3\text{Te}_4\text{Br}$ . This is achieved in a way that Figure 2 exhibits in two perspective projections, down  $[010]$  and  $[100]$ , respectively.

**Figure 2.** Two views of the connections of the  $\text{La}_3\text{Te}_{14}\text{Br}_4$  building blocks to the three-dimensional structure of  $\text{La}_3\text{Te}_4\text{Br}$ ; projections down  $[010]$  (top) and  $[100]$  (bottom).



The crystal structure of  $\text{La}_3\text{Te}_4\text{Br}$  is a derivative of the structure of  $\text{U}_3\text{Te}_5$  [27]. The latter has a remarkably smaller unit cell, owing to the mixed-valence nature of  $\text{U}_3\text{Te}_5 = (\text{U}^{3+})_2(\text{U}^{4+})(\text{Te}^{2-})_5$ , with both  $\text{U}^{3+}$  and especially  $\text{U}^{4+}$  considerably smaller than  $\text{La}^{3+}$ .

Meanwhile, we have obtained a number of  $\text{RTeI}$  type telluride-iodides, for example  $\text{PrTeI}$  which belongs to the  $\text{PbFCl}$ -type of structure [28].

### 3. Experimental Section

All reactions and handling were carried out under a dry nitrogen atmosphere using dry box equipment (MBraun, Garching, Germany).  $\text{LaBr}_3$  was prepared following the ammonium bromide route and purified as described previously [29-32].  $\text{LaTe}$  was synthesized from a 1:1 molar ratio of  $\text{La}$

powder (Chempur, Karlsruhe, Germany, 99.9%) and Te granules (Sigma-Aldrich, München, Germany, 99.99%). The present single crystals were obtained from a reaction of LaTe (150 mg, 0.56 mmol), LaBr<sub>3</sub> (150 mg, 0.40 mmol) and Ir (90 mg, 0.47 mmol). The starting materials were filled into He-arc welded tantalum ampoules jacketed with an evacuated silica tube to prevent oxidation at high temperatures. The following temperature program was applied in a tubular furnace: heated to 1,323 K with 50 K/h, kept at that temperature for 24 hours, then cooled slowly to 1,223 K (2 K/h) and annealed for 248 hours, then cooled to 973 K with 5 K/h, kept there for 1 hour, and cooled to room temperature over 8 hours. The tantalum tube was transferred to a dry-box and the contents inspected with the aid of a microscope.

La<sub>3</sub>Te<sub>4</sub>Br forms well-faceted, polygonal black crystals. These were selected under a microscope and sealed in thin-walled glass capillaries. After their quality had been checked by Laue diffraction patterns, the single crystals were transferred to a single-crystal X-ray diffractometer (Stoe Image Plate Diffraction System, IPDS I) to collect a complete intensity data set at ambient temperature. Structure solution and refinement was performed with the programs SHELXS-97 (direct methods) [33] and SHELXL-97 [34], scattering factors were from International Tables for X-ray Crystallography [35]. Data corrections were carried out for Lorentz and polarization factors and absorption (numerical with the aid of the programs X-RED [36] and X-SHAPE [37]). Further details of the crystal structure determination may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (fax: (+49)7247-808-666; e-mail: crysdata@fizkarlsruhe.de), on quoting the depository number ICSD-380475, the authors and the journal citation.

Crystal data for La<sub>3</sub>Te<sub>4</sub>Br (1007.04 g mol<sup>-1</sup>); diffractometer IPDS-I, Stoe, Darmstadt; Mo-K<sub>α</sub> (graphite monochromator, λ = 71.073 pm); T = 293(2) K; 2θ<sub>max</sub> = 56.3°; 100 images, 0° ≤ φ ≤ 200°; Δφ = 2°; indices: -21 ≤ h ≤ 21, -5 ≤ k ≤ 5, -18 ≤ l ≤ 18; transmission (min, max) = 0.0307, 0.0929; ρ<sub>calc</sub> = 6.596 g cm<sup>-3</sup>; 9390 reflection intensities measured of which 1318 were symmetrically independent, R<sub>int</sub> = 0.0571, F(000) = 1656, μ = 27.547 mm<sup>-1</sup>. Orthorhombic, Pnma (no. 62), a = 1634.3(2), b = 435.0(1), c = 1426.6(2) pm, V = 1014.1(2) 10<sup>6</sup> pm<sup>3</sup>, Z = 4. R values: R<sub>1</sub>/wR<sub>2</sub> for 1120 reflections with [I<sub>0</sub> > 2σ(I<sub>0</sub>)]: 0.0349/0.0920 and for all data: 0.0426/0.0965; S<sub>all</sub> = 1.072.

#### 4. Conclusions

The first lanthanide telluride bromide, La<sub>3</sub>Te<sub>4</sub>Br, was obtained from LaTe and LaBr<sub>3</sub> (in the presence of iridium metal which has no effect on the formation of La<sub>3</sub>Te<sub>4</sub>Br) at elevated temperatures. The black crystals crystallize with a variant of the U<sub>3</sub>Te<sub>5</sub> type of structure with dicapped trigonal prisms (2 × LaTe<sub>7</sub>Br and LaTe<sub>6</sub>Br<sub>2</sub>, respectively) connected via common faces and edges to a three-dimensional structure. La<sub>3</sub>Te<sub>4</sub>Br is best considered as a valence compound according to (La<sup>3+</sup>)<sub>3</sub>(Te<sup>2-</sup>)<sub>4</sub>(Br<sup>-</sup>).

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